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Electron and hole transport in poly(fluorene-benzothiadiazole)

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We investigate the electron and hole transport in poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT). An Ohmic hole contact on F8BT is achieved by using the high work function anode MoO_3 as hole injection contact, enabling the occurrence of space-charge limited currents. The electron transport in F8BT is trap-limited and the traps can be deactivated using *n*-type doping by decamethylcobaltocene (DMC). Due to the alignment of the energy levels of DMC and F8BT the electrons from the DMC donor not only fill the traps but also fill up the lowest unoccupied molecular orbital of F8BT such that the electron transport can be enhanced beyond the hole transport. © *2011 American Institute of Physics*. [doi:10.1063/1.3574907]

Fluorene-based conjugated polymers are attractive as active material in polymer light-emitting diodes (PLEDs).[1,2] They combine high quantum efficiencies with thermal stability, insensitivity to photo-oxidation, and their physical parameters as solubility and processibility can be tuned through chemical modification and copolymerization. With an alternation of poly(fluorene-2,7-diyl) (F8) and benzothiadiazole (BT) units, poly(9,9-dioctylfluorene-alt-BT) (F8BT) has been intensively utilized for PLED applications exhibiting high quantum and power efficiencies as a green emitter.[3–5] One of the most interesting properties of this class of polymers is the ability to form a liquid crystalline phase which leads to an increase in the carrier mobility in the alignment direction.[6,7] Next to PLEDs, F8BT is also used as active electron donating material in polymer/polymer solar cells, where it is blended with other fluorene based copolymers.[8–12] Furthermore, F8BT has a relatively high electron affinity (~3.3 eV) and a large ionization potential of ~5.9 eV. As a result it can also be used as an electron-acceptor in all-polymer bulk heterojunctions.[13,14] Regarding charge transport F8BT shows a relative high electron field-effect mobility of $\sim 10^{-3}$ $cm^2/V\,s$.[15] Together with its good luminescent properties F8BT is a good candidate for light-emitting field-effect transistors.[16] In diode structures, relevant for PLEDs and OPV blends, the charge transport of F8BT has not been extensively studied. Investigations of the hole transport properties are hindered by the large hole injection barrier from common electrodes as Au or PEDOT:PSS, due to the deep highest occupied molecular orbital (HOMO). As a result measured current-voltage characteristics are injection limited and do not provide information on the hole mobility. Regarding electron transport the intrinsic electron mobility in conjugated polymers is often masked by the presence of traps, giving rise to trap-limited currents. In a recent study by Steyrleuthner *et al.*[17] the electron transport in F8BT diodes was modeled using the exponentional trapping model, with a typical trap width of about 100 meV. On the other hand, Blakesley *et al.*,[18] showed that the electron transport in F8BT can also be well described without trapping sites, using a Gaussian disorder model with 100 meV disorder, so similar to the width of trap energies as used in Ref. 17, showing that it is very hard to disentangle the two mechanisms. In the present study we determine the electron and hole mobilities in diodes of F8BT. The hole injection problem can be solved by using molybdenum trioxide (MoO_3) as an anode. It was recently demonstrated that MoO_3 forms an Ohmic hole contact on poly(9,9-dioctylfluorene), which has a similar HOMO level as F8BT.[19] The presence of an Ohmic contact leads to a space-charge-limited current (SCLC), which allows a direct determination of the hole mobility. With regard to the electron transport in poly(2-methoxy-5–2-ethylhexyloxy-1,4-phenylenevinylene) (MEH-PPV) we recently demonstrated that the electron traps can be deactivated by addition of the *n*-type dopant decamethylcobaltocene (DMC).[20] By filling the traps with electrons from the DMC donor a trap-free space-charge limited electron current can be obtained in MEH-PPV, enabling a direct measurement of the free electron mobility. In this study *n*-type doping by DMC is not only used to deactivate the traps that limit the current in undoped F8BT, but also to enhance the electron transport beyond the trap-free space-charge limited current.

The F8BT polymer was purchased from Sigma-Aldrich and for spin coating *o*-xylene was used as a solvent. To study the hole transport in F8BT hole-only devices were fabricated which consisted of glass with structured ITO substrates and as bottom electrode PEDOT:PSS was used. After spin coating the F8BT with a thickness of 74 nm a top electrode of 10 nm of MoO_3 was evaporated as the hole injection contact and was subsequently capped with 100 nm of Al. All the hole-only diodes are measured in an inert-gas environment and a positive bias is defined such that holes are injected from the top MoO_3 electrode. In Fig. 1 the *J-V* characteristics of F8BT hole-only devices using MoO_3 as the injecting electrode are shown for various temperatures.

For a complete description of the SCLC the charge carrier density dependence- and field dependence of the mobility need to be taken into account. The experimental data were fitted with a numerical drift-diffusion model[21] in which the density p and field dependence E are described by[22]

$$\mu_p(T,p,E) \approx \mu_p(T,p) f(T,E), \tag{1}$$

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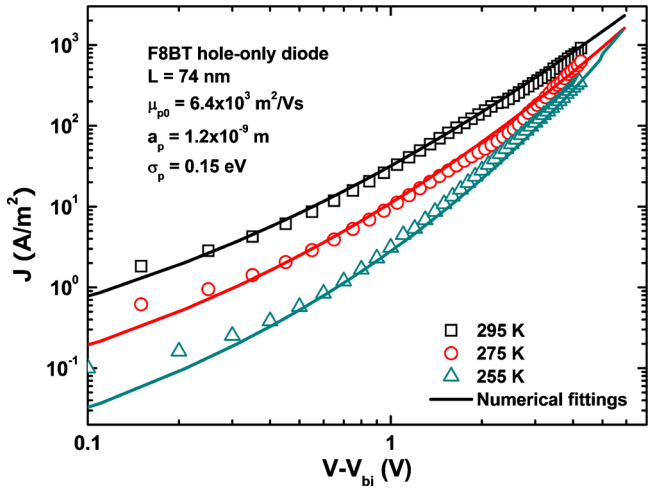

FIG. 1. (Color online) *J-V* characteristics of a F8BT hole device using an Ohmic MoO_3 top contact at various temperatures. The solid lines are numerically calculated currents incorporating a density- and field-dependent mobility.

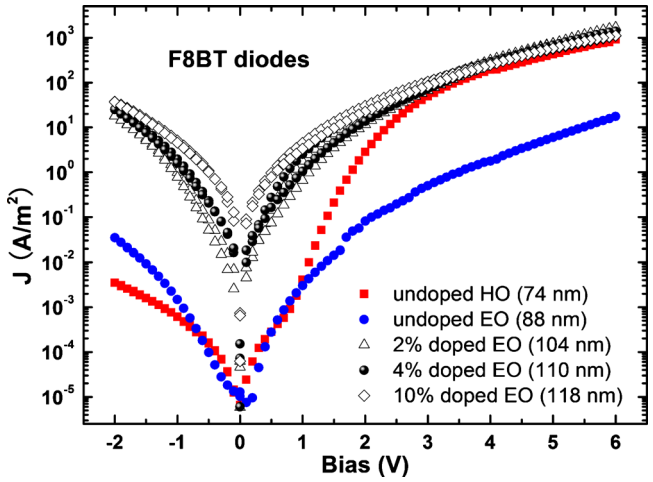

FIG. 2. (Color online) *J-V* characteristics of F8BT hole-only and electron-only devices. Upon *n*-type doping the electron current at low bias is much larger than the hole current, demonstrating the increase in the free electron concentration upon doping with the DMC donor.

$$\mu_p(T,p) = \mu_0(T)\exp\left[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})\left(2\frac{p}{N_t}\right)^{\delta}\right], \quad (2)$$

$$\delta = 2\frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln[\ln(4)]}{\hat{\sigma}^2}, \quad (3)$$

$$f(T,E) = \exp\left[0.44(\hat{\sigma}^{3/2} - 0.22)\left\{\sqrt{1 + 0.8\left(\frac{Eea}{\sigma}\right)^2} - 1\right\}\right], \quad (4)$$

where $\mu_0(T)$ is the mobility in the limit of zero charge carrier density and electric field, $\hat{\sigma} \equiv \sigma / k_B T$ and σ is the width of the Gaussian density of states (DOS), N_t the density of transport sites and $a = N_t^{-1/3}$ the intersite distance. At room temperature a hole mobility μ_h of 3×10^{-10} $m^2/V\,s$ is obtained. As shown in Fig. 1, the temperature dependence is described by using μ_{p0} of 6.4×10^3 $m^2/V\,s$, a_p of 1.2 nm, and σ_p of 0.15 eV. Similar values for σ were recently found for other polyfluorene derivatives.[19,23]

The poor electron transport in many conjugated polymers as poly(2-methoxy-5–3,7-dimethyloctyloxy-p-phenylene vinylene) (OC_1C_{10}-PPV) has been explained by the presence of traps with an exponential distribution of trapping sites in energy.[24] The weak temperature of the trap-limited electron current could be explained by incorporating the presence of a Gaussian DOS for free electrons.[25] However, modeling of the electron currents alone is not sufficient to determine the intrinsic electron mobility as well as the total amount of trap states and their position inside the band gap. We recently demonstrated that the traps can be deactivated by addition of the *n*-type dopant DMC.[20] By filling the traps with electrons from the DMC donor a trap-free space-charge limited electron current can be obtained in MEH-PPV, enabling a direct measurement of the intrinsic electron mobility. Here, we employ the same method to investigate the electron transport in F8BT. To investigate the electron transport as a function of *n*-type doping electron-only devices are fabricated with the (doped) F8BT layers sandwiched between an environmentally oxidized Al anode (30 nm) and a 5 nm Ba cathode capped with 100 nm Al. The F8BT layer was spin-coated from *o*-xylene and acetonenitrile was used to dissolve DMC, which is subsequently blended with the F8BT solution. The *J-V* characteristics of F8BT electron-only devices with various concentrations of DMC are shown in Fig. 2. With increasing doping concentration we observe at low voltages a strong increase in the electron current over several orders of magnitude. As a reference also the density-voltage (*J-V*) characteristics of a PEDOT:PSS/F8BT/MoO_3/Al hole-only device is shown. As a first observation we see that the electron current of the undoped F8BT is lower than the hole current, but the difference (two orders of magnitude) is less than in the PPV derivatives (four orders of magnitude). Apparently, the electron trapping is less severe in F8BT. Furthermore, we observe that starting from a 2 wt % doping ratio the electron current density exceeds the intrinsic hole current at low voltages and keeps on increasing at higher doping density. This is in contrast with the behavior observed in MEH-PPV, where the doped electron current saturated on top of the hole current.[20] At higher voltage the *J-V* characteristics saturate for increasing doping. This is the regime where the injected carriers overwhelm the background concentration due to doping and the current becomes space-charge limited. The fact that the *J-V* characteristics of the doped electron-only devices of F8BT exceed the hole current and not saturate like in MEH-PPV can be understood by considering the energy band diagram in Fig. 3. For MEH-PPV the HOMO of the DMC donor (3.3 eV) is located below its LUMO (2.9 eV) [Fig. 3(a)], such that electrons from the donor can only fill the deep electron traps. Due to the energy offset of 0.4 eV the donor cannot supply electrons to the LUMO of MEH-PPV, such that the electron current of doped MEH-PPV will not exceed the SCL hole current. For F8BT, however, the LUMO is located at 3.3 eV and thus aligns with the HOMO of the DMC dopant [Fig. 3(b)]. As a result, the electrons of DMC not only fill the traps, but also donate electrons to the LUMO. As a result, a strong increase in the *J-V* characteristics can be observed at low voltages, due to the Ohmic currents from the background electron density due to *n*-type doping.

For the doped samples the SCLC at high voltages can be modeled using the same parameters as obtained for the hole transport. This demonstrates that also for F8BT the hole and electron transport are identical. The undoped trap-limited

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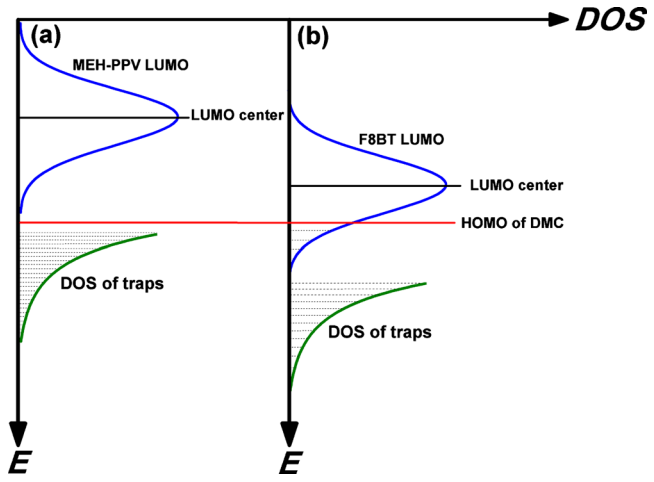

FIG. 3. (Color online) Schematic depiction of the energy-level alignment of a Gaussian DOS (LUMO) for the transport of free electrons and an exponential DOS for electron traps. (a) For MEH-PPV the LUMO is higher than the DMC HOMO and electron from DMC can only fill the traps. (b) For F8BT with a LUMO at 3.3 eV the electrons from the DMC dopant can in addition to filling the traps also fill part of the Gaussian DOS.

electron current then can be modeled using an effective trap density $N_{t(\mathrm{eff})}$ of 7.5×10^{23} m^{-3} and a trap distribution temperature T_t of 780 K. The electron transport in DMC-doped EO devices can be calculated by adding an additional free electron background density n_0 due to doping,[20] shown in Fig. 4(a). The total ionized electron density n_0+n_{t0}, where n_{t0} equals the amount of traps filled at zero bias by the doping, and free electron density (n_0) can then be calculated as a function of the doping concentration, shown in Fig. 4(b). We obtain that n_0 is on the order of $\sim10^{22}$ m^{-3}. Similar to

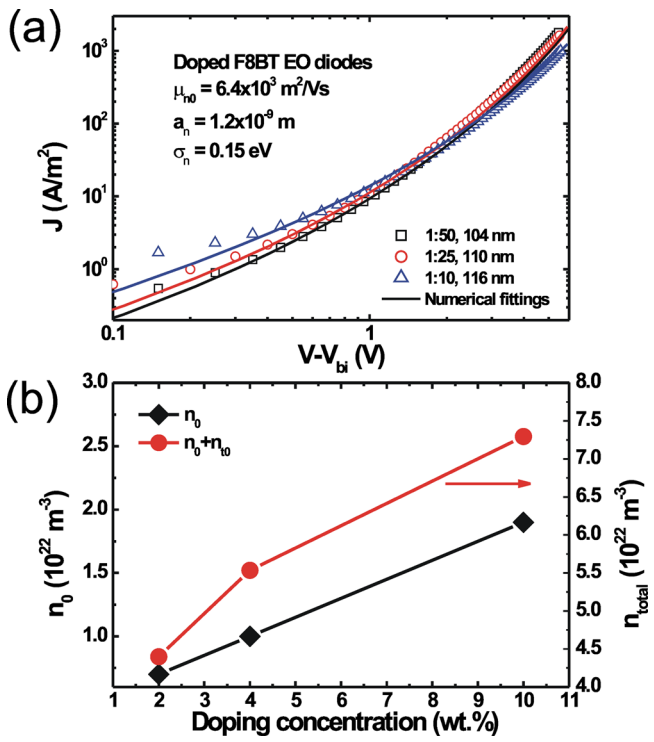

FIG. 4. (Color online) (a) Trap-free electron currents upon n-type doping together with numerically calculated J-V characteristics (lines). (b) Total ionized and "free" electron densities as a function of doping concentration.

MEH-PPV only a relatively small fraction of typically 4% of the DMC dopants is ionized. These results show that similar to the hole currents by p-type doping,[26] also the electron currents in a conjugated polymer can be enhanced beyond the SCL current by doping in solution processed layers, when the energy levels of the dopant and host are well aligned.

In conclusion, the hole and electron transport in poly [(9,9-di-n-octylfluorenyl-2,7-diyl) - alt - (benzo[2,1,3] thiadiazol-4,8-diyl)] (F8BT) have been characterized. Using MoO_3 as a hole injection contact a space-charge limited current can be obtained, that enables us to determine the hole mobility. With DMC as n-type dopant not only the electron traps can be filled, but also free electrons in the LUMO of F8BT can be induced. As a result at low voltages the electron transport in F8BT can be strongly enhanced beyond the hole transport by n-type doping.

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